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# First-Principle Simulations Of Water

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# First-Principle Simulations of water

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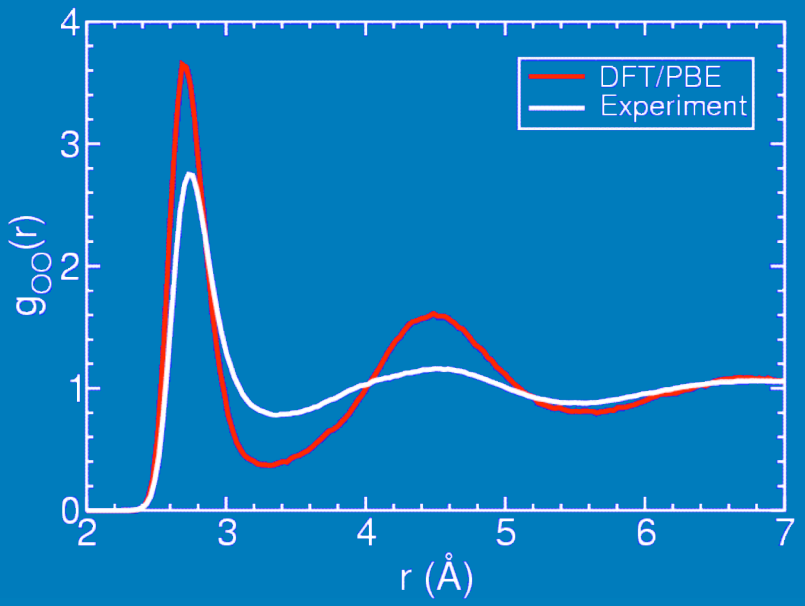
# What's wrong with DFT/GGA water?

- Well converged DFT/GGA simulations of water at 300 K are severely over-structured
- Diffusion is too slow by at least a factor of ten

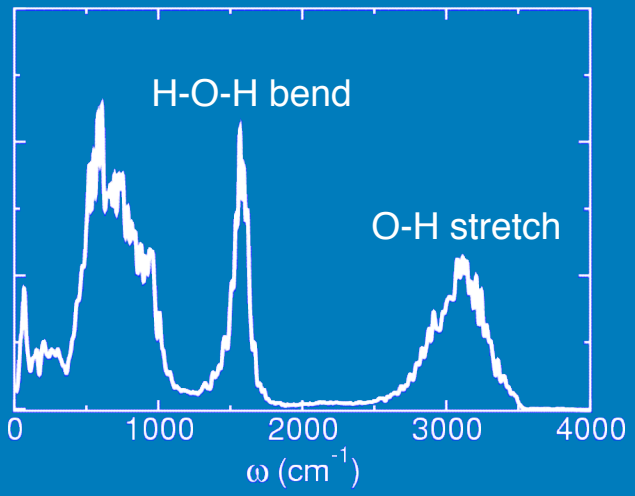
- Possible reasons:
  - Importance of quantum effects
  - Inaccuracies in DFT/GGA functionals




J.C. Grossman, *et al*. JCP **120**, 300 (2004)

# How important are quantum effects in water?

- O-H stretch and H-O-H bend are in the range of 1000 to 3500 $cm^{-1}$




- At a temperature of 300 K $k_B T \sim 300\ cm^{-1}$

$$k_B T \ll h/2\pi$$

- Intramolecular vibrations are highly quantum mechanical
- At T=300K, only the ground state will be populated
- Quantum and classical models will have very different energy distributions

I.G. Tironi, *et al.* Chem. Phys. Lett. **250**, 19 (1996)

# Quantum effects can be accounted for with path integral methods

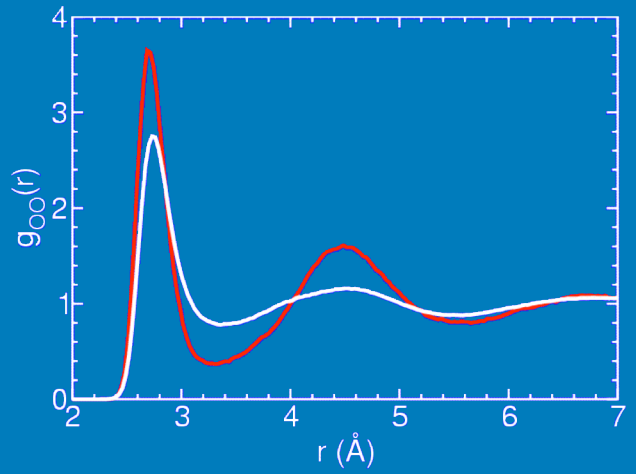
- Path integral sampling of water with empirical potentials:
  - **ST2**: JCP **82**, 5164 (1985)
  - **SPC/F**: JCP **106**, 2400 (1997)
  - **TIP4F, TIP5P**: JCP **115**, 10758 (2001)
  - **MCDHO**: JCP **115**, 7622 (2001)

- All empirical simulations have found quantum effects decrease the structure of water
- Appears to be similar to an increase in the classical simulation temperature
  - Often cited as being approximately equivalent to a 50° increase in simulation temperature

R.A. Kuharski and P.J. Rossky, J. Chem. Phys. 82, 5164 (1985)

# Can quantum effects account for all of the overstructure?

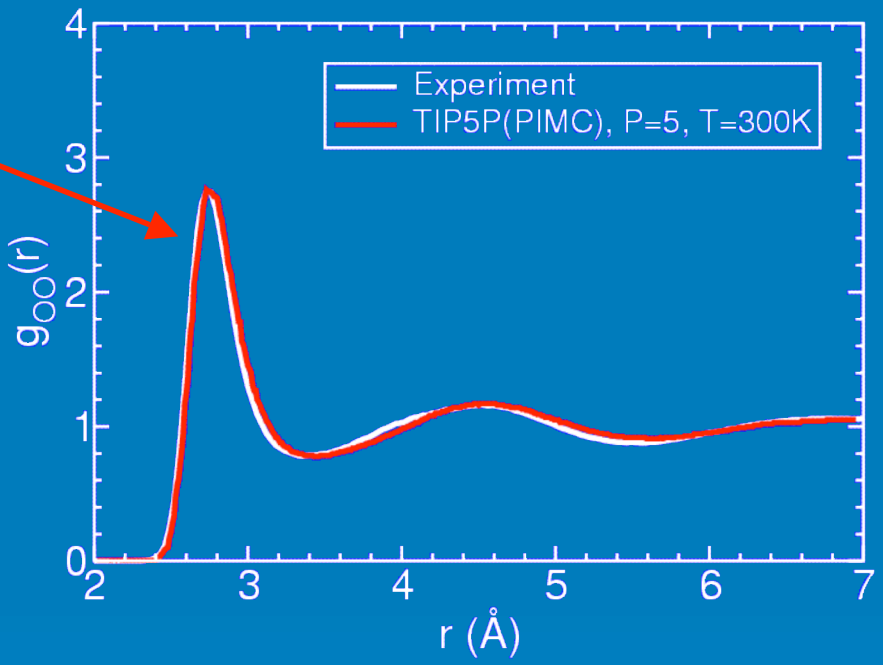
- The amount of softening is different for each potential
- Consistent comparisons are difficult
  - Most empirical potentials already include quantum effects implicitly through parameterization
- Some notable exceptions:
  - TIP5P(PIMC) potential was parameterized to reproduce experimental data when used *with* path integral sampling




M.W. Mahoney and W.L. Jorgensen, J. Chem. Phys. **115**, 10758 (2001)

# TIP5P(PIMC) potential

- The path integral sampling with the TIP5P(PIMC) potential in excellent agreement with experiment at 300K

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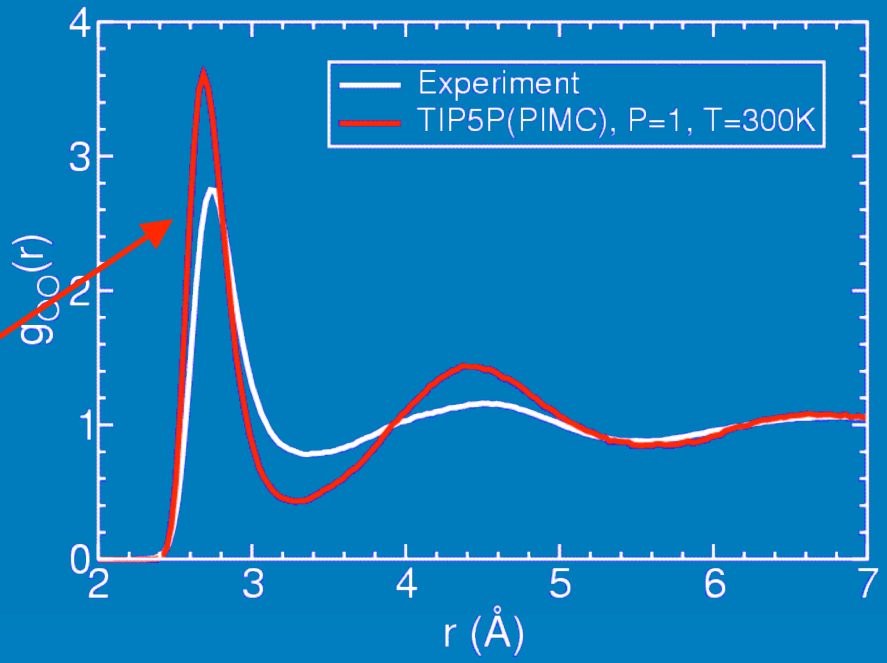
- The path integral sampling with the TIP5P(PIMC) potential in excellent agreement with experiment at 300K
- Without PI sampling TIP5P(PIMC) becomes overstructured at 300K




Diffusion ~10x slower than exp.

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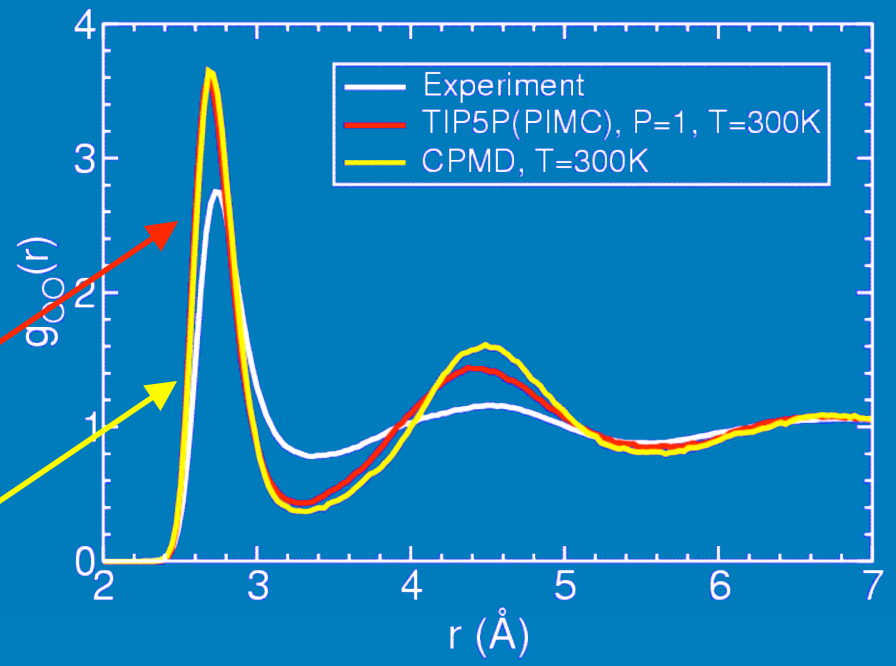


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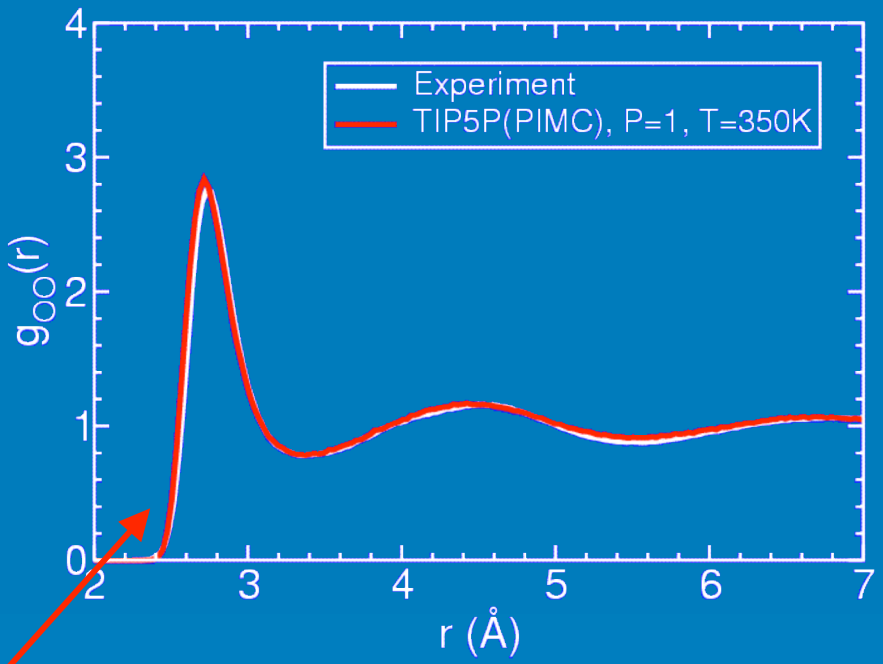
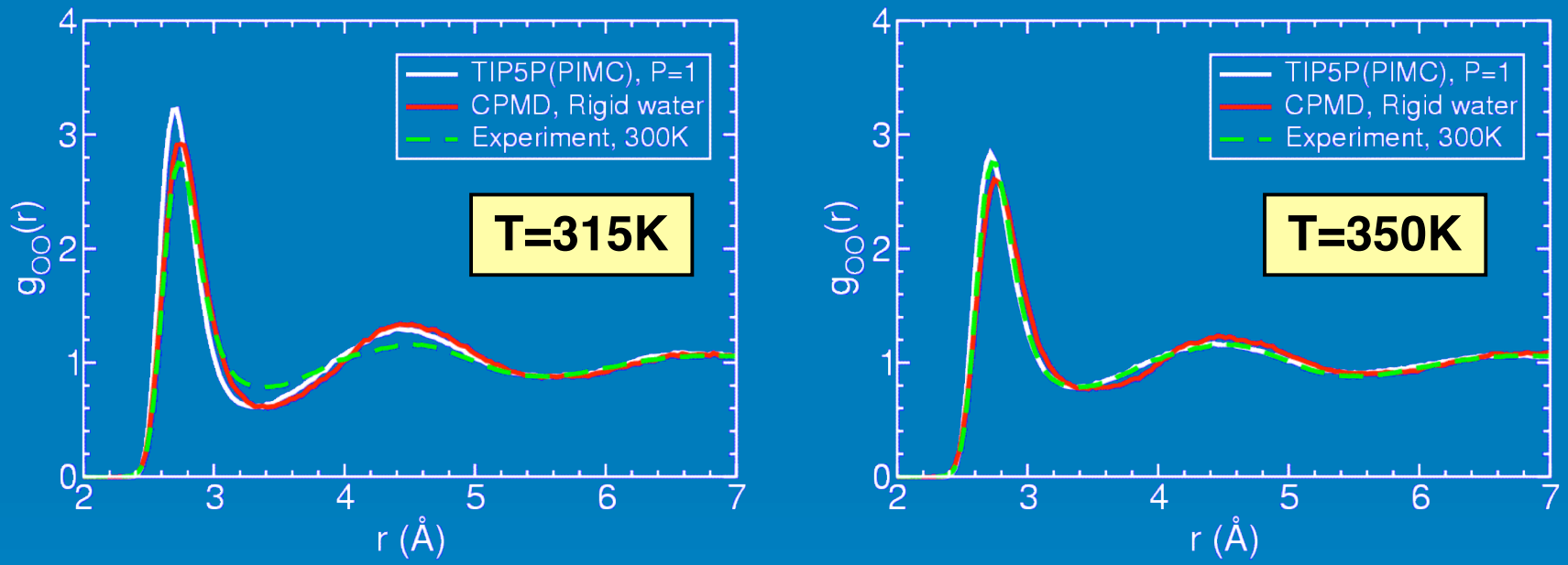
- The path integral sampling with the TIP5P(PIMC) potential in excellent agreement with experiment at 300K
- Without PI sampling TIP5P(PIMC) becomes overstructured at 300K
- The amount of overstructure is very similar to DFT/GGA
- TIP5P(PIMC) without PI sampling at 350K restores agreement with experiment



# DFT/PBE rigid water as a function of T

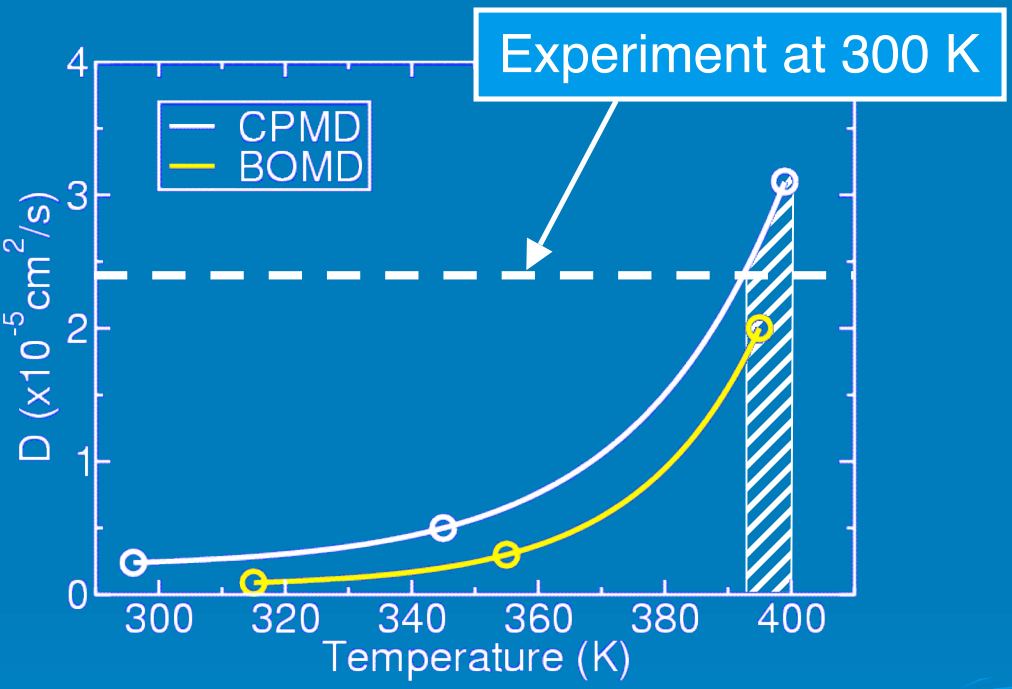



- The rigid water model within DFT/PBE is very similar to TIP5P(PIMC), P=1
- At 350 K, DFT/PBE rigid water is in good agreement with experiment

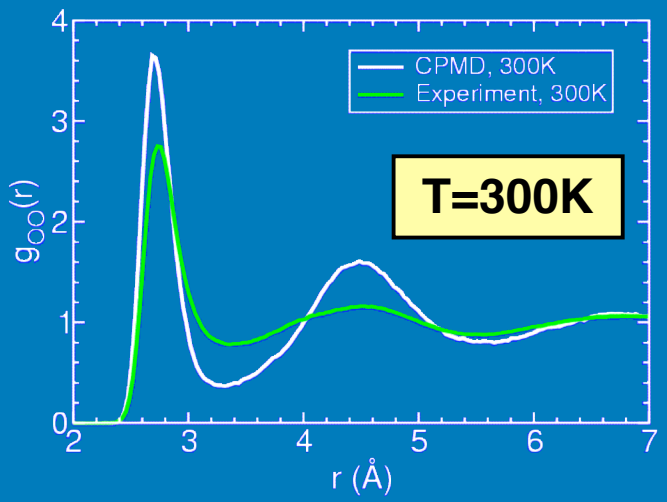
M. Allesch, et al. J. Chem. Phys. 120, 1 (2004)

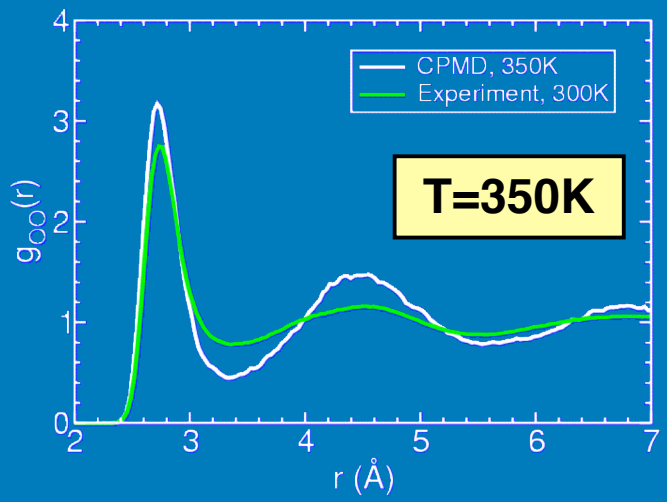
# DFT/PBE flexible water as a function of T

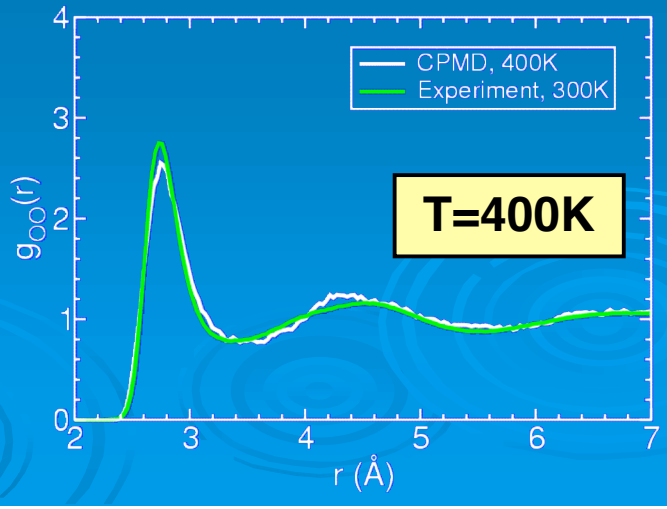
- Diffusion coefficients for DFT/PBE flexible water increase slowly with temperature
- T = 390 to 400 K needed to approach the 300 K experimental diffusion
- Preliminary results indicate small differences between CPMD and BOMD diffusion



# DFT/PBE flexible water as a function of T

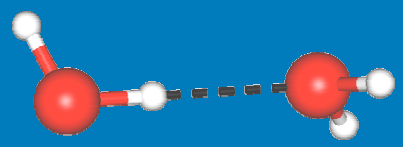



- DFT/PBE flexible water approaches experiment as temperature is increased to ~ 400 K

# A variety of DFT/GGA functionals work well for the water dimer



| | $r_{OO}$ (Å) | $D_e$ (kcal/mol) | $\alpha_{iso}$ (Å$^3$) | |
|---|---|---|---|---|
| PBE | 2.90 | -5.11 | 1.59 | GGA |
| BLYP | 2.95 | -4.18 | 1.58 | GGA |
| PBE1 | 2.90 | -4.98 | 1.41 | Hybrid |
| B3LYP | 2.93 | -4.57 | 1.45 | Hybrid |
| Exp. | 2.95 | -5.44 | 1.43 | |

- Geometry and binding energy are accurately reproduced within DFT/GGA
- Moderate improvement in polarizability when going from simple GGAs to hybrid functionals that include Hartree-Fock exchange

X. Xu and W.A. Goddard III, J. Phys. Chem. A **108**, 2305 (2004)

# Conclusions

- Overstructure and slow diffusion in DFT/GGA water may be related to:
  - Tendency of the GGA to overestimate polarizabilities
  - Neglect of quantum effects
- In the immediate future:
  - DFT/GGA simulations of water should be performed at elevated temperatures
- In the long term:
  - Hybrid functionals should be considered
  - Convergence of path integral sampling with DFT needs to be fully explored

B. Chen, I. Ivanov, M.L. Klein and M. Parrinello PRL 91, 215503 (2003)

# Simulation Details

- Norm-conserving pseudopotentials
- Plane wave basis truncated at 85 Ryd.

- Car-Parrinello simulations:
  - 54 water molecules
  - fictitious mass of 340 au
  - Time step of 0.07 fs
- Born-Oppenheimer simulations:
  - 64 water molecules
  - 12 electronic iterations per step
  - Time step of 0.24 fs